The Explosion Spectra of the Alkaline Earth Metals

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By ARTHUR L. BECKER

ABSTRACT

Modification of Anderson's exploded wire source of light.—In 1920 Anderson obtained extremely high temperature spectra of certain metals by discharging a large condenser through fine metal wires. The authors have found that the metal wire may be replaced by an *asbestos fiber saturated with an aqueous solution of a salt* of the chosen metal. Thus the explosion spectrum of any soluble salt may be obtained. The fiber is uninjured by the explosion and may be used repeatedly. With a 6-foot grating, from six to twenty explosions are necessary for a first-order spectrogram. The condensers (0.3 M.F.) were charged to 40,000 volts through a high resistance with the rectified current from a 1-kilowatt transformer, and were discharged by means of a special switch. The apparatus and connections are described. The temperature of the explosion is probably about 15,000° C. and the pressure 10 to 20 atmospheres.

Explosion spectra of chlorides of Ba, Ca, Mg, and Sr, λ 2280–λ 4550.—When lines due to impurities, Cu, Zn, Al, Pb, C, and N, are eliminated, the spectra are found to be almost pure spark spectra, consisting chiefly of the doublets of the first and second subordinate series, $2p-md$ and $2p-ms$. Of the arc lines, only the fundamental singlet line, $1S-2P$, appears and its intensity with reference to the spark lines is only one-tenth as much as in the vacuum arc and about the same as in the spectra of the solar chromosphere and of class B stars. The first member of the Bergman doublet series of Mg, $3d-4f$, λ 4481, appears and also a line of Ba, λ 4350, whose series relation is unknown. No lines of Cl, H, or O were detected. The prominence of impurity lines shows how small an amount of material is needed to give explosion spectra.

Relation of explosion spectra to the theory of spectra.—According to Saha's theory, the metals used would be ionized at the expense of the less readily ionized Cl, H, and O; in fact at 15,000° C. the alkali earths should be almost completely ionized. Hence, according to Sommerfeld, the explosion spectra should be almost pure spark spectra. These conclusions agree with the facts. The faint arc lines may be emitted during the initial and final stages of the explosion. The Bergman line indicates an approach toward double ionization.

I. INTRODUCTION

In 1920 Dr. J. A. Anderson[1] announced a new method of producing spectra. This method consists of exploding a short fine wire of the metal chosen by discharging through the wire a large condenser charged to several thousand volts. If the explosion takes place in a confined space an absorption spectrum is produced; while if the explosion occurs in the open air or in a partial vacuum the spectrum partakes more of the nature of an emission spectrum. The exact type of spectrum produced depends, however, upon other factors besides the pressure.

[1] *Astrophysical Journal*, 51, 37, 1920.

One of the interesting features of this source of light is that it enables a very powerful stimulus to be applied very abruptly to the molecules of an element. It is thus possible to study spectra under conditions widely different from those obtaining in most laboratory sources.

In the course of some investigations with these explosions, which have been briefly reported elsewhere,[1] a modification of Anderson's source was announced. The fine wire used by Anderson is replaced by a fine asbestos fiber which is saturated with a solution of some salt of the desired metal. When the high tension condensers are discharged through this saturated fiber, with the fiber in the open air, an emission spectrum is obtained characteristic of the metallic ions in the solution.

It is the purpose of this paper to discuss the spectra produced by exploding, in this manner, solutions of the alkali earth metals.

II. THE APPARATUS

The apparatus, as used, differed in several minor respects from that described by Anderson. Changes were made with a view to greater convenience and efficiency and are perhaps worth describing briefly.

The condensers were built up of sheets of double strength window glass, $10 \times 12.5''$, alternating with sheets of roofing tin, $8 \times 10''$. The tin sheets were pressed and their edges carefully smoothed. Tabs on the corners of the tin sheets projected alternately on either side of the pile and were bolted together. The condensers were built up in piles of sixteen tin plates and firmly tied with cord. Sixteen such piles were constructed. The condensers thus obtained were placed in pairs in large glass battery jars and covered with transil oil. The total capacity thus obtained was of the order of 0.3 M.F. The advantage of such a condenser is that its units are readily portable and easily repaired in case of rupture—no small advantage in the present work since the voltages used were near the rupture voltage of the dielectric and transient surges sometimes resulted disastrously to the glass plates.

The charging voltage was obtained from a 50,000-volt 1-kilowatt transformer. The primary of this transformer was fed with a 110-

[1] *Science*, 54, 305, 1921.

volt alternating current obtained from the 200-volt alternating current power line of the university by use of a second transformer. The second transformer was employed to protect the university power circuits from the possibility of high frequency transient surges. Rectification was obtained by means of a 100,000-volt 100-milliampere kenotron.

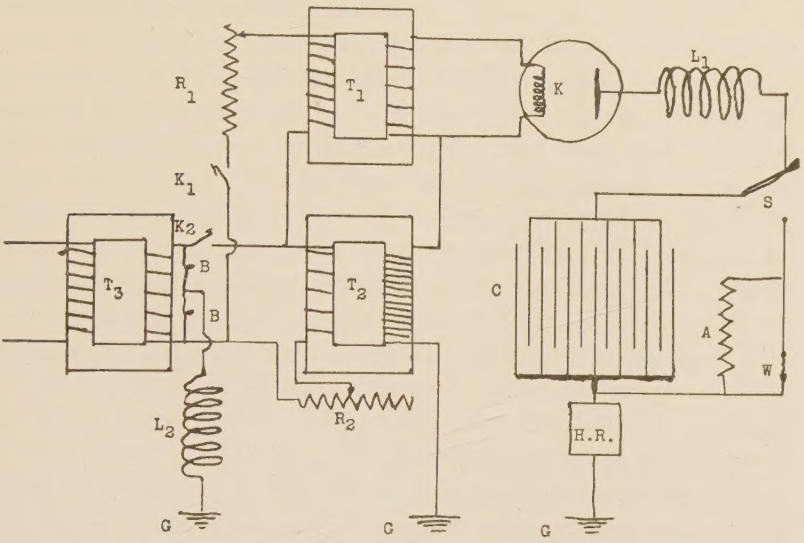

FIG. 1

The discharge circuit was closed by means of a heavy single pole, single throw-knife switch immersed in transil oil. A heavy spring served to close this switch rapidly. It was held open by a trigger device while the condensers were charging. A lever was arranged so that a single pull released the trigger holding the switch open, opened the primary circuit of the high voltage transformer, and opened the high-voltage charging circuit.

The electrical circuit is shown diagrammatically in Figure 1. The features described above will be noted. There is shown, also, a water rheostat which was used to keep down the charging current and protect the kenotron. The water rheostat consisted of a glass tube, about 5 mm bore and 120 cm long. Its resistance was so high that several seconds were required to charge the condensers.

The leak resistance, A, was made from a piece of No. 30 Nichrome wire about 3 m long. It allowed any absorbed charge on the condensers or any charge that did not escape in the first surge across the asbestos fiber to leak off gradually. Its resistance, 65 ohms, was sufficiently high so that only an inappreciable part of the first surge escaped through it.

The inductances, L_1 and L_2, consisted merely of twenty-five turns of wire. They were intended to act as choke coils to stop any high frequency oscillations. To reduce further the possibility of damage by high frequency oscillations a 220-volt carbon lamp, B, was shunted across each half of the secondary of the transformer, T_3, between the ground and the outside terminals.

The fibers were supported on an insulating stand which could be adjusted both vertically and laterally by rack-and-pinion movements. The upper end of the fiber was held in a brass clamp on the stand while the lower end rested against a brass finger.

The spectra were photographed with a 6-foot concave grating, Rowland mounting. The first-order spectrum was used, with a dispersion of 9.4 A per mm. A region of about 700 A could be photographed on the plates employed.

The explosions were focused on the slit with a quartz or glass lens, as the spectral region demanded. The adjustment was made as described by G. A. Hemsalech.[1] A light was placed behind the fiber to illuminate it and the image of the illuminated fiber was focused on the slit by the aid of the vertical and lateral adjustments of the fiber mounting. It is difficult to make this adjustment with great accuracy and so a rather wide slit had to be used. A wide slit was useful also in reducing the number of explosions necessary.

III. PROCEDURE

To take a spectrogram the fiber was saturated with an aqueous solution of some salt of the desired metal; the fiber was focused on the slit as described, the switch S opened, and the high-tension lead attached to it by a spring clip; and the switches K_1 and K_2 closed. A few seconds were allowed for the condensers to charge. The lever was then pulled which simultaneously opened the switch

[1] *Philosophical Magazine*, 40, 37, 1920.

K_2 and released the trigger on S. As the blade of S descended, the spring clip of the high-tension lead was pulled off. When the switch closed, the charge of the high-tension condenser was discharged through the fiber, with a sharp crack and a brilliant flash. The fiber was uninjured by these discharges and could be moistened and the procedure repeated. From six to twenty such explosions were required, the number varying with the spectral region.

The copper arc was used as a comparison to aid in the identification of the spectra. The copper arc was particularly useful in this work as copper, from the brass clamps that hold the fiber, is the principal impurity in the spectra. The plates were measured on a small comparator and the wave-lengths computed to tenths of angstroms. Greater accuracy was rendered difficult by the character of the lines; because of the width of the slit and because of the high pressure and gaseous velocities in the explosion, the lines were rather broad. The problem, however, was principally one of identification and the accuracy attained was sufficient for that.

IV. DATA

By the use of aqueous solutions of their chlorides, photographs were taken of the spectra of calcium, magnesium, barium, and strontium. The region λ 2280–λ 4550 was completely covered for calcium, while of this range the region λ 3381–λ 3890 for magnesium and barium, and λ 3381–λ 4550 for strontium was not covered.

The chief impurities in the spectrograms are copper and zinc from the brass clamps, as mentioned. There also appeared the strong aluminum pair, λ 3944 and λ 3961, the lead line at λ 4058, carbon at λ 2479, and nitrogen at λ 3995 and λ 4447. A striking fact is that in the spectrum obtained from a salt of any one of the four metals used there always appear many of the strong lines of the other three and of cadmium which is also a member of this group of metals. Although no great effort was made to secure purity of the salts used, the other metals of the group could have been present in the solutions only in very minute quantities. This source seems to be effective in producing spectra of substances which are present in the solution only in extremely low concentrations. It is of interest to note that no lines due to the acid radical employed, chlorine, nor

any lines of hydrogen or oxygen have been identified. If any radiations of these elements were produced, their intensities were too low to register with the exposures used.

The wave-lengths of calcium, magnesium, barium, and strontium, remaining after the elimination of the known impurities,

TABLE I

WAVE-LENGTHS IN EXPLOSION SPECTRA OF THE ALKALI EARTHS

$CaCl_2$		$MgCl_2$		$SrCl_2$		$BaCl_2$		IDEN.	TRUE WAVE-LENGTH
Wave-Length	Intensity	Wave-Length	Intensity	Wave-Length	Intensity	Wave-Length	Intensity		
2585.8	0	.....	.....	.....	.....	.....	.....	?	
2592.6	0	.....	.....	.....	.....	.....	.....	?	.....
2606.5	0	.....	.....	.....	.....	.....	.....	?	.....
2612.7	0	.....	.....	.....	.....	.....	.....	?	.....
2630.7	1	.....	.....	.....	.....	.....	.....	?	.....
2739.3	1	.....	.....	.....	.....	.....	.....	?	.....
2756.0	1	2755.7	1	2755.8	1	.....	.....	?	.....
2790.8	3	2790.8	5	2790.8	5	2790.8	4	Mg	2790.80
2796.5	10	2796.5	12	2796.8	12	2796.7	10	Mg	2795.53
2802.8	8	2802.7	8	2802.6	7	2802.8	6	Mg	2802.69
2852.6	1	2852.2	1	2852.2	1	.....	.....	Mg	2852.13
2928.6	2	2928.6	2	2928.6	1	.....	.....	Mg	2928.64
2936.9	3	2936.8	2	2936.8	1	.....	.....	Mg	2936.76
3107.5	1	.....	.....	.....	.....	.....	.....	?	.....
3126.5	1	.....	.....	.....	.....	.....	.....	?	.....
3159.0	13	3159.0	6	3159.0	5	.....	.....	Ca	3158.88
3180.7	17	3180.8	8	3180.7	7	.....	.....	Ca	3181.27
3380.7	8	3381.0	1	3381.0	8	.....	.....	Sr	3380.8
3706.1	10	.....	.....	.....	.....	.....	.....	Ca	3706.03
3737.0	12	.....	.....	.....	.....	.....	.....	Ca	3736.91
.....	.....	.....	.....	.....	.....	3891.9	15	Ba	3891.79
3933.7	25	.....	.....	.....	.....	.....	.....	Ca	3933.67
3968.5	20	.....	.....	.....	.....	.....	.....	Ca	3968.48
.....	.....	.....	.....	.....	.....	4078.0	10	Sr	4077.75
.....	.....	.....	.....	.....	.....	4130.7	20	Ba	4130.68
4212.0	2	.....	.....	.....	.....	4166.0	7	Ba	4166.02
4215.9	1	.....	.....	.....	.....	.....	.....	?	.....
.....	.....	.....	.....	.....	.....	4215.6	7	Sr	4215.52
4226.7	3	4227.0	1	.....	.....	4226.7	4	Ca	4226.72
.....	.....	.....	.....	.....	.....	4350.4	3	Ba	4350.38
4481.0	7	4481.1	15	.....	.....	.....	.....	Mg	4481.17
.....	.....	.....	.....	.....	.....	4525.1	7	Ba	4524.95
.....	.....	.....	.....	.....	.....	4554.0	30	Ba	4554.04

are tabulated in Table I. Here are listed for each salt used the wave-lengths obtained, and the intensity, source, and exact wave-length in International Units of each line. It will be noted that there are several unidentified lines, chiefly in the shorter wave-

lengths. It was impossible to identify these lines with the alkali earths or any of the impurities detected. As they may be due to any of a half-dozen or more elements, nothing can be said at this time as to their source.

V. DISCUSSION OF DATA

It will be noted that after the impurity and unidentified lines have been eliminated, strikingly few lines remain. This fact

TABLE II

DOUBLET SERIES OF THE EARTH ALKALIES*

First Subordinate Series $2p_1-md_2$
$2p_1-md_1$
$2p_2-md_2$

Element Ordinal Number	Mg		Ca		Sr		Ba	
	Wave-Length	Intensity	Wave-Length	Intensity	Wave-Length	Intensity	Wave-Length	Intensity
3	.....	.....	.....	.....	.....	.....	7485.4	x
	.....	.....	8498.3	x	10038.3	x	8564.0	x
	2798.0	12	8542.5	x	10328.3	x	or	
	2790.8	5	8662.5	x	10915.0	x	10635.6	x
	.....	.....	.....	.....	.....	.....	10052.4	x
	.....	.....	.....	.....	.....	.....	12084.8	x
4	.....	.....	3181.4	17	3475.0	x	4166.2	7
	1737.5	x	3179.5	17	3464.6	x	4130.9	20
	1734.7	x	3159.0	13	3380.9	8	3892.0	15
5	.....	.....	.....	.....	2324.6	a	2641.5	a
	.....	.....	2113.0	x	2322.5	a	2634.9	a
	.....	.....	2103.5	x	2282.3	a	2528.5	a

Second Subordinate Series $2p_1-ms$
$2p_2-ms$

Element Ordinal Number	Mg		Ca		Sr		Ba	
	Wave-Length	Intensity	Wave-Length	Intensity	Wave-Length	Intensity	Wave-Length	Intensity
1	2795.5	12	3933.8	25	4077.9	10[c]	4554.2	30
	2802.7	8	3968.6	20	4215.7	7[c]	4934.2	x
2	2928.6	2	3706.2	10	4161.9	x	4525.2	7
	2936.5	2	3737.1	12	4300.6	x	4900.1	x
3	1753.3	x	2208.9	x	2471.7	a	2771.6	a
	1750.6	x	2198.0	x	2423.7	a	2647.4	a

[c] = On barium plate.

* These values are taken from Fues, *Annalen der Physik*, 63, 1, 1920.

becomes even more striking when the lines of the alkali earth metals which do appear are classified according to their series relationships, as is done in Table II. In this table a number in the intensity column opposite a wave-length shows the relative intensity with which the line appeared; an "*a*" indicates that it did not appear on the plate, while an "*x*" indicates that the line lies in a region not photographed in this work. Comparison of the lines in Table II with those in Table I shows that, with one exception in the case of barium, one in calcium, and two in magnesium, all of the lines are members of the first and second subordinate series of the respective metals.

It will be seen that the first two members of each series for each metal appear, if they lie in the region photographed. In the few cases where higher members of the series lie in the region covered, they did not appear on the photograph—probably because of the usual decrease in intensity with increasing ordinal number in series.

Such a spectrum for the alkali earths is of course wholly different from that produced by ordinary laboratory sources. In the usual spark spectrum, members of the triplet and singlet series appear with intensities of the same order as those of the lines of the doublet series. (See for example the tables V and VI of this paper.) Nelthorpe,[1] however, using metallic salts in a discharge tube, obtained results for calcium, barium, and strontium quite similar to these in the region λ 6500–λ 3400.

VI. CORRELATION OF DATA AND THEORY

The explanation of such a spectrum as has been described above is readily found in the modern theories of atomic structure and spectral emission. Bohr has pointed out that, due to quantum changes of one of its outer electrons, a neutral atom will emit a spectrum which is called the "arc" spectrum. An ionized atom, however, has an effective nuclear charge $+2e$ now acting on the outer electron, instead of $+e$ as in the former case, and will consequently emit a totally different spectrum known as the "spark" spectrum.

Sommerfeld[2] has stated in his "Verschiebungssatz" that the "spark" spectrum of any element is similar in series structure to the

[1] *Astrophysical Journal*, 41, 16, 1915.

[2] Sommerfeld, *Atombau und Spektrallinien*, 3d ed., chap. vi.

"arc" spectrum of elements in the preceding column of the periodic table. He has further pointed out that for the alkali earths the "spark" spectrum consists of the lines of the doublet series, while the triplet and single line series comprise the "arc" spectrum. The "arc" spectrum of the alkalies, then, consists of doublets, while the "spark" spectrum of the alkalies is a complicated spectrum without known series, similar to the spectra of the noble gases. Laboratory evidence in support of the "Verschiebungssatz" has been rather meager. Goldstein,[1] by means of a powerful excitation, succeeded in producing spectra of the alkalies, in which the usual doublet spectra were entirely missing, and which by their complexity, resembled the spectra of the noble gases. It seemed, therefore, that he had not only succeeded in producing the "spark" spectrum of the alkalies, but in doing so had so completely ionized the emitting atoms that the "arc" spectrum was wholly absent. For the alkalies, it was then possible to produce at will either the "arc" or the "spark" spectrum.

The spectra produced in these experiments, it will be seen, then, are almost pure "spark" spectra of the alkali earths. They do for the alkali earths what Goldstein did for the alkalies. They show that it is possible to produce for these metals the "spark spectrum" with practically no trace of the "arc" lines.

It is possible to carry farther the application to the spectra at hand of the quantum theory of emission. In the source under discussion a considerable energy, 50 calories or so, was applied to 1 or 2 milligrams of material. The effect was to heat the material very quickly to an extreme temperature, estimated by Anderson at 20,000° in his case. This heating is so abrupt and its dissipation so rapid that it seems not unreasonable to say that the emission takes place principally, if not entirely, at this high temperature. The reason for thinking this to be the case will be apparent later.

Dr. M. N. Saha in several recent papers has discussed the temperature radiations of gases.[2] Saha's work has been amended

[1] *Verh. d. D. Phys. Ges.*, **10**, 321, 1907.

[2] *Philosophical Magazine*, **41**, 267, 1921, and *Proceedings of the Royal Society*, Series A, **99**, 135, 1921.

and extended by Russell[1] and Milne.[2] The conclusions of these writers would seem to be applicable to the explosion spectra. In brief they are as follows (to a large extent Saha's wording is followed).

An atom, cool and unstimulated, has its vibrating electron in the $1s$-orbit. Such an atom or mass of atoms does not emit and can absorb only lines of the principal series, $v = 1s - mp$. If the atoms are heated, the vibrating electron proceeds toward ionization through the various quasi-stationary states and radiation occurs. First we have emission of $1s - 2p$ lines and then of $1s - mp$ or principal series. When the gas emits the line $1s - 2p$ strongly it can absorb the lines of the $2p - md$ and $2p - ms$, diffuse and sharp series. At a higher temperature, the $2p - md$ and $2p - ms$ lines begin to be emitted and the $3d - 4f$ or fundamental series can be absorbed. Thus, as the heating of the atoms continues, the electron proceeds toward ionization, being able progressively to absorb and to emit series corresponding to higher and higher levels of energy.

The theory is not sufficiently developed to permit the calculation of the proportion of atoms in the various quasi-stationary states but the qualitative situation is clear. The temperature at which the fundamental line $1s - 2p$ is emitted and the $2p$-orbits commence to form will be higher, the higher the ionization potential of the element. Other orbits appear at temperatures intermediate between this temperature and the temperature at which ionization is complete. At any state, the proportion of atoms at any energy level will be smaller, the higher the quantum number corresponding to this stage. Thus the $1s - 2p$ and $1s - mp$ series will be the first to appear, the last to disappear, and the most intense always. The $2p - md$, $2p - ms$, and other series will appear later, disappear sooner, and be weaker. The disappearance of $1s - 2p$ marks complete ionization.

After the first step ionization is completed, if heating of the mass of atoms continues, the singly ionized atoms then proceed toward double-ionization through the same cycle of processes described for the un-ionized atoms. The series in question will of course now

[1] *Astrophysical Journal*, 55, 119, 1922.

[2] *Observatory*, 46, 261, 1921.

be the series of the "spark" spectrum. As before, the series emitted will afford an index of the energy conditions of the mass of atoms.

Although it is impossible to compute the proportion of atoms in various stages, Saha has pointed out that the proportions of ionized and un-ionized atoms may be computed on the basis of modern thermodynamics by the aid of the Nernst theorem of the reaction-isochore. The equation for computing the percentage of ionization is

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{4.571\, T} + 2.5 \log T - 6.5 ,$$

where x is the fraction of atoms ionized, P, the gaseous pressure, T, the temperature, U, heat of dissociation, or calories to ionize one gram-atom.

Also

$$U = \frac{eVN}{J\ 300} = 2.302 . 10^4\ V \text{ calories} ,$$

where e is charge on the electron, V, ionization potential in volts, J, mechanical equivalent of heat, N, Avogadro's number.

The percentage of ionization is determined by the pressure, temperature, and ionization potential and may readily be computed.

Table III gives for the alkali earths the values of the ionization potential and of the heat of dissociation.

TABLE III

Element	Ionization Potential	U in Calories
Magnesium	7.65	1.761×10^5
Calcium	6.12	1.409×10^5
Strontium	5.7	1.313×10^5
Barium	5.12	1.178×10^5

Table IV gives the values computed by Saha for the percentage of ionization of the alkali earths at a pressure of one atmosphere at various temperatures.

Saha has extended his theory to second-stage ionization also. Corrections to his formulae have been pointed out by Russell and

by Milne (*loc. cit.*). The extent of second-stage ionization, however, need not be considered here since the spectroscopic criteria of such ionization are as yet unknown.

Russell (*loc. cit.*) has shown that if atoms of several kinds are heated together it is possible to compute the fraction of each kind ionized at any temperature and pressure. In general it may be said that if an element is more easily ionized than the average, its percentage of ionization will be greater than if it alone were present. For elements whose ionization potential is greater than the average, the reverse will be the case.

TABLE IV

Temperature of Element	Mg	Ca	Sr	Ba
5000	5.10^{-2}	2	3.2	5.5
6000	2	8	13	19
7000	6	23	32	43
8000	17	46	58	70
9000	34	70	79	85
10,000	56	85	90	93
11,000	75	93	95	.....
12,000	86	96.5	97.5	.....
13,000	93	98.5	98.5	.....
14,000	96	Complete Ionization		
15,000	98			
16,000	99			

It is now possible, at least qualitatively, to apply the theory discussed above to the spectra under consideration. The solutions used were aqueous solutions of chlorides of the alkali earths. The effect of the explosions was to dissociate these chlorides and the water and to heat the resultant atoms to a high temperature. Since hydrogen, oxygen, and chlorine each have higher ionization potentials than any of the alkali earth metals, the alkali earths were ionized at the expense of these other constituents and to a greater extent than they would have been if the material exploded had consisted of an equal amount of the pure metals. The effect of the explosion is not wholly one of temperature—the electric effects, however, probably act to further the work of the temperature.

The exact temperature and pressure obtained are, of course, unknown. Anderson estimated from the intrinsic brilliancy that the temperature attained was of the order of 20,000° C. From two

different considerations he inferred that the pressure attained from an explosion in a slot in a block of wood was of the order of 20 atmospheres. Since the explosions here discussed took place in the open air, both pressure and temperature were probably somewhat less, although the voltage used, 40,000 volts, was higher than that used by Anderson. It must be remembered, moreover, that in the case of the exploded solutions the pressure to be used in computing the degree of ionization of an element is the partial pressure of that element which is much less, of course, than the total pressure of the explosion. It is probably safe to assume that throughout these experiments, the temperature attained and the partial pressure of the major constituents were in each case of the same order of magnitude. That is, we deal here with spectra of the alkali earths produced all under approximately the same conditions.

Examination of Table IV will show that at a temperature of 15,000° and a pressure of one atmosphere, ionization of each of the alkali earths is practically complete. At higher temperatures or lower pressures the certainty of complete ionization is, of course, greater. These figures are chosen in the belief that they are at least of the right order of magnitude.

Spectroscopic evidence that complete ionization had been attained in these explosions would be the complete suppression of the "arc" spectrum and the appearance of only the "spark" spectrum. As pointed out above, the last arc line to disappear is $1S-2P$; its disappearance indicates complete ionization. For the alkali earths the fundamental line, $1S-2P$, of the single line spectra has the following value for the various elements:

Magnesium	2852.13
Calcium	4226.72
Strontium	4607.34
Barium	5535.69

The line λ 4226.72 is the only calcium line in Table I which is not a member of either the first or second subordinate doublet series. Its intensity, 3, is only one-eighth that of the fundamental doublet pair, λ 3968 and λ 3934. The weakness of λ 4227 and the absence of all other "arc" lines, shows how nearly all radiation takes place from ionized atoms.

In the magnesium spectrum are only two lines which do not appear among the doublets of Table I. One of these lines is the fundamental singlet line, λ 2852, which appears with one-tenth the intensity of the fundamental doublet pair. The other line, λ 4481, is the unresolved first member of the Bergman doublet series, $3d-4f$. Its emission, as pointed out above, denotes the presence of radiating atoms in an even higher energy state than the atoms which emit the sharp and diffuse series.

The lines $1S-mP$ of strontium and barium unfortunately do not lie in the region photographed in this work. However, these lines, if they appeared, would be expected to be relatively fainter even than the corresponding lines of calcium and magnesium (since the heats of dissociation of strontium and of barium are less than those of calcium and magnesium). The appearance of the line, λ 4350, the only barium line, not in the sharp or diffuse doublet series, is puzzling. This has been classed as an "arc" line of barium; that is, its intensity is greater in the ordinary arc than in the spark. It does not seem to have been fitted into any of the known barium series and, therefore, no criterion exists for explaining its appearance.

With the exception of the barium line, λ 4350, the explosion spectra of the alkali earths consist of the fundamental singlet line, $1S-2P$, and of the doublet or "spark" lines. There would seem to be two possible explanations of the persistence of the fundamental "arc" line. First, the pressure and temperature conditions may not be sufficiently extreme to produce complete ionization. In this case it is evident that conditions in the explosion source as here used must be similar to those pointed out by Saha[1] as existing in class A2, A, B9, B8 stars; that is, calcium and magnesium are almost wholly ionized although λ 4227 of calcium still persists. The second possible explanation is that, since we start with our material to be exploded at a normal temperature and the final temperature and pressure cannot be built up instantly, some of the radiation of the neutral atom may appear while the atoms are being brought to their final ionized condition. If so, then, as pointed out above, the lines $1S-2P$ will predominate in the arc spectrum.

[1] *Proc. Roy. Soc.*, A, **99**, 135, 1921.

The effect of electrolytic dissociation, which of course exists in the solution used, somewhat complicates the situation. It is hard to say what effect the electronic rearrangements of dissociation may have on the radiation produced. Some evidence on this point is afforded by some spectrograms taken of the explosions of fine magnesium and calcium wires. The results so obtained are wholly similar to the results with exploded solutions of magnesium and calcium. In general the $1S-2P$ line is not so much weakened

TABLE V

IONIZATION OF MAGNESIUM

Source	Intensity of λ 2795–λ 2803	Intensity of λ 2852	Ratio of Intensities
King's electric furnace	.....	1200	.....
Crew and McCauley arc	8	10	0.8
Eder and Valenta spark	10	8	1.2
Fowler vacuum arc	50	30	1.7
Exploded wire	10	2	5.0
Exploded solution	10	1	10.0

TABLE VI

IONIZATION OF CALCIUM

Source	Intensity of λ 3933–λ 3968	Intensity of λ 4226	Ratio of Intensities
King's electric furnace	55	1000	.05
Crew and McCauley arc	400	500	.8
Lockyer spark	500	400	1.2
Loving vacuum arc	20	8	2.5
Exploded wire	10	2	5.
Exploded solution	25	3	8.
Chromosphere of sun	72	8	9.
Stars of type B	7	1	7.

in the exploded wire spectra as in the exploded solution. This fact may be due, however, to the lower partial pressure of the metal and the smaller amount of material exploded in the solution; both of these factors would tend toward more complete ionization. The effect of dissociation would then appear to be negligible.

For the purposes of comparison there are given in tables V and VI data on the ratio of the intensities for different sources of the fundamental spark doublet, $1s-2p$, to the fundamental arc singlet $1S-2P$, for calcium and for magnesium. This ratio is, as pointed

out above, an index of the degree of ionization produced in any emitting source. It will be noted that ionization is carried farther in the exploded solution than in the other sources, and that the ionization produced in the exploded solution compares with that in the sun and stars of class B.

In conclusion it may be pointed out that the exploded solution as source, discussed above, must contain a relatively small percentage of un-ionized atoms. Only the fundamental single lines $1S-2P$ and the barium line, λ 4350, appear of the "arc" spectrum and these lines are faint. It, of course, follows from Saha's theory that there must also be slight emission of other arc lines. This emission was, however, too weak to be detected by the means at hand.

Further studies of the spectra produced by this type of discharge are now being carried on.

VII. SUMMARY

1. A modification of Anderson's exploded wire as source of light is developed, in which there is exploded, in place of the wire, an aqueous solution of any salt of the desired metal. The method is thus made applicable to any metal, rather than only to those which can be obtained in the form of fine wires.

2. The application of this source to the alkali earth metals produced for these metals an almost pure "spark" spectrum.

3. The correlation of this data with Sommerfeld's "Verschiebungssatz" and with Saha's theories of the temperature radiation of gases is discussed. The data afford corroboratory evidence for both these theories.

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